EXHIBIT D

ANALYTICAL METHODS

SECTION I

INTRODUCTION

Inorganic Methods Flow Chart: Figure 1 outlines the general analytical scheme the Contractor shall follow in performing analyses under this contract.

Permitted Methods: Any analytical method specified in Exhibit D may be used as long as the documented instrument or method detection limits meet the Contract Required Detection Limits (Exhibit C). Analytical methods with higher detection limits may be used only if the sample concentration exceeds five times the documented detection limit of the instrument or method.

Initial Run Undiluted: All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range (as appropriate), re-analysis for that analyte(s) is required after appropriate dilution. The Contractor shall use the least dilution necessary to bring the analyte(s) within the valid analytical range (but not below the CRDL) and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proof that dilution was required to obtain valid results, both diluted and undiluted sample measurements must be contained in the raw data. ICP data showing a high concentration for a particular analyte, combined with an analyte result that is close to the middle range of the calibration curve in the diluted sample, constitute sufficient proof that the sample had to initially be run diluted for that analyte on a furnace AA instrument. All sample dilutions shall be made with deionized water appropriately acidified to maintain constant acid strength.

Quality Assurance/Quality Control Measurements: The Contractor is reminded and cautioned that Exhibit D is a compendium of required and/or permitted analytical methods to be used in the performance of analyses under this contract. The quality assurance/quality control procedures or measurements to be performed in association with these methods or analyses are specified in Exhibit E. In the event references to quality assurance measurements in any of the methods appear to be in conflict with or to be less stringent than the requirements of Exhibit E, the requirements of Exhibit E will prevail.

Raw Data Requirements: The Contractor is reminded and cautioned that the collection and provision of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance Protocol of Exhibit E. The Raw Data Deliverables requirements are specified in Exhibit B, Section II.C.2.d. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate provisions of Exhibit B.

Glassware Cleaning: Lab glassware to be used in metals analysis must be acid cleaned according to EPA's manual "Methods for Chemical Analysis of Water and Wastes" or an equivalent procedure.

Standard Stock Solutions: Stock solutions to be used for preparing instrument or method calibration standards may be purchased or prepared as described in the individual methods of Exhibit D. All other solutions to be used for quality assurance/quality control measurements shall conform to the specific requirements of Exhibit E.

Aqueous Sample pH Measurement: Before sample preparation is initiated on an aqueous sample received in shipment, the Contractor shall check the pH of the sample and note in a preparation log if the pH is <2 for a metals sample or if the pH is >12 for a cyanide sample. The Contractor shall not perform any pH adjustment action if the sample has not been properly preserved. If the sample has not been properly preserved, contact SMO before proceeding with the preparation and analysis for further instructions.

Sample Mixing: Unless instructed otherwise by the EPA Administrative Project Officer or Technical Project Officer, all samples shall be mixed thoroughly prior to aliquoting for digestion. No specific procedure is provided herein for homogenization of soil/sediment samples; however, an effort should be made to obtain a representative aliquot.

Background Corrections: Background corrections are required for Flame AA measurements below 350 nm and for all Furnace AA measurements. For ICP background correction requirements, see Exhibit D Section IV, Part A, paragraph 2.0.

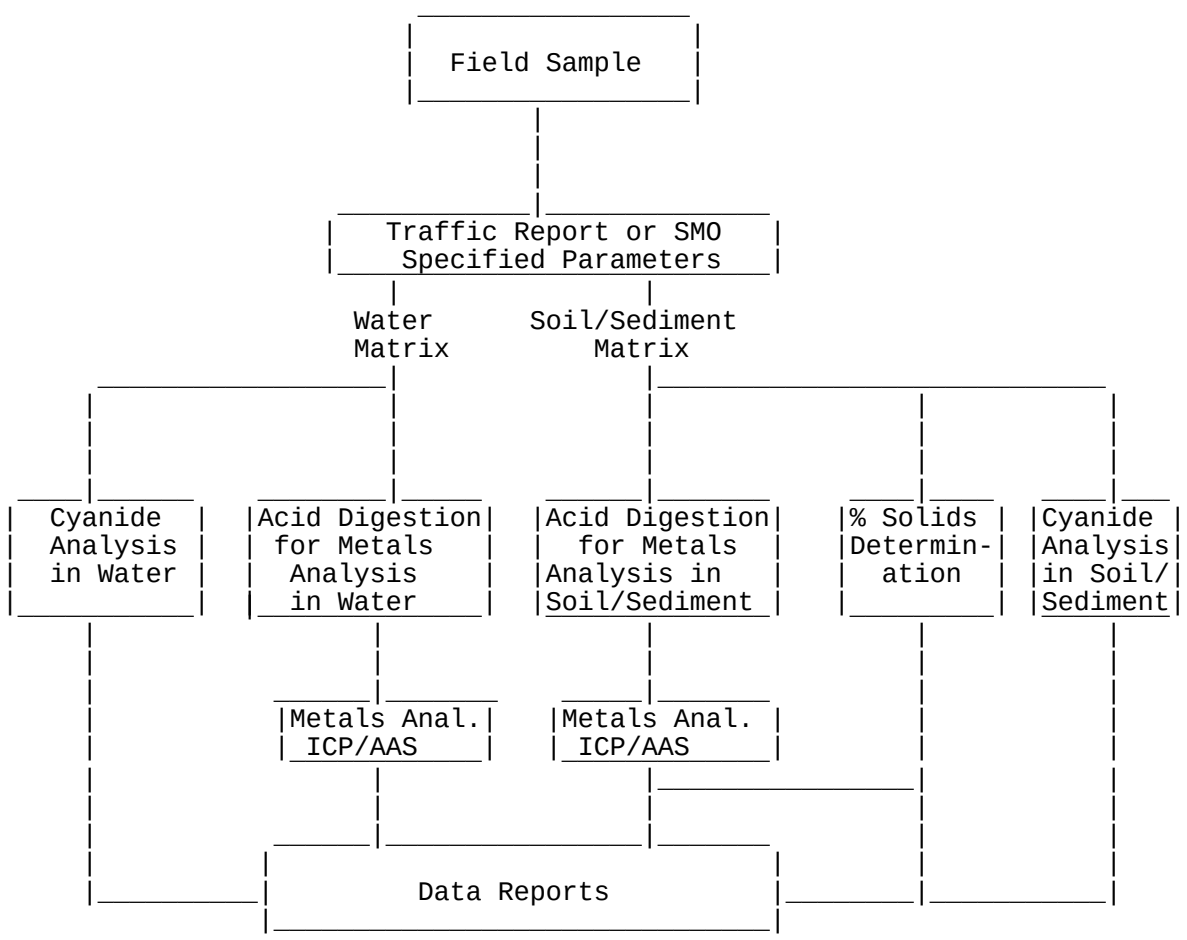
Replicate Injections/Exposures: Each furnace analysis requires a minimum of two injections (burns), except for full method of standard addition (MSA). All ICP measurements shall require a minimum of two replicate exposures. Appropriate hard copy raw data for each exposure/injection shall be included in the data package in accordance with Exhibit B, Section II, Part C, paragraph 2.d. The average of each set of exposures/injections shall be used for standardization, sample analysis, and reporting as specified in Exhibit D.

Dissolved Metals: If dissolved metals are requested by the EPA Regional offices, the Contractor shall follow the instructions provided on the Traffic Report(s). If there are no instructions on the Traffic Report, the Contractor shall digest the samples designated as dissolved metals.

If the Regional office indicates on the Traffic Report that a digestion is not to be performed when analyzing field samples for dissolved metals, then an aqueous laboratory control sample (LCS) and a post-digestion (hardcopy Form 5B and diskette QC codes PDO and PDF) spike sample are not required.

Figure 1

INORGANICS METHODS FLOW CHART



SECTION II

SAMPLE PRESERVATION AND HOLDING TIMES

A. SAMPLE PRESERVATION

1. Water Sample Preservation

Measurement Parameter	Container(1)	Preservative(2)
Metals	P,G	HNO_3 to pH <2
Cyanide, total and amenable to chlorination	P,G	0.6g ascorbic acid(3) NaOH to pH >12 Cool, maintain at 4°C(±2°C) until analysis

FOOTNOTES:

(1) Polyethylene (P) or glass (G).
(2) Sample preservation is performed by the sampler immediately upon sample collection.
(3) Only used in the presence of residual chlorine.

2. Soil/Sediment Sample Preservation

The preservation required for soil/sediment samples is maintenance at 4°C (± 2°) until analysis.

B. HOLDING TIMES FOR WATER AND SOIL/SEDIMENT SAMPLES

Following are the maximum sample holding times allowable under this contract. To be compliant with this contract, the Contractor shall analyze samples within these times even if these times are less than the maximum data submission times allowed in this contract.

Analyte	No. of Days Following Sample Receipt by Contractor
Mercury	26 days
Metals (other than mercury)	180 days
Cyanide	12 days

SECTION III

SAMPLE PREPARATION

A. WATER SAMPLE PREPARATION

1. Acid Digestion Procedure for Furnace Atomic Absorption Analysis

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL heating vessel, add 1 mL of (1+1) HNO_3 and 2 mL 30% H_2O_2 to the sample. Cover with watch glass or similar cover and heat on a steam bath, hot plate or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

If Sb is to be determined by furnace AA, use the digestate prepared for ICP/flame AA analysis.

2. Acid Digestion Procedure for ICP and Flame AA Analyses

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL heating vessel, add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a steam bath, hot plate or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

B. SOIL/SEDIMENT SAMPLE PREPARATION

1. Acid Digestion Procedure for ICP, Flame AA and Furnace AA Analyses

a. Scope and Application

This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

Aluminum	Chromium	Potassium
Antimony	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

b. Summary of Method

A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb and the Flame AA or ICP analysis of Al, As, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the Furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, T1, V, and Zn. A separate sample shall be dried for a percent solids determination (Section IV, Part F).

c. Apparatus and Materials

(1) 250 mL beaker or other appropriate vessel

(2) Watch glasses

(3) Thermometer that covers range of 0^{o} to $200^{o}C$

(4) Whatman No. 42 filter paper or equivalent

d. Reagents

(1) ASTM Type II water (ASTM D1193): Water must be monitored.

(2) Concentrated nitric acid (sp. gr. 1.41)

(3) Concentrated hydrochloric acid (sp. gr. 1.19)

(4) Hydrogen Peroxide (30%)

e. Sample Preservation and Handling

Soil/sediment (nonaqueous) samples must be refrigerated at $4^{o}C$ ($\pm 2^{o}$) from receipt until analysis.

f. Procedure

(1) Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01g) a 1.0 to 1.5 g portion of sample and transfer to a beaker.

(2) Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 92-$95^{o}C$ and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3,

replace the watch glass, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel.

(3) After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the hot plate or equivalent heating source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.

(4) Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.)

(5a) If the sample is being prepared for the furnace AA analysis of Sb or the flame AA or ICP analysis of Al, As, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of Type II water, return the covered heating vessel to the hot plate or equivalent heating source, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is now ready for analysis.

(5b) If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, T1, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute the sample to 100 mL with Type II water (or centrifuge the sample). NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted digestate solution contains approximately 2% (v/v) HNO_3. Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

g. Calculations

(1) A separate determination of percent solids must be performed

(Section IV, Part F).

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

Where,
C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample
S = % Solids/100

C. TOTAL METALS SAMPLE PREPARATION USING MICROWAVE DIGESTION

1. SCOPE AND APPLICATION

This method is an acid digestion procedure using microwave energy to prepare water and soil samples for analysis by GFAA, ICP, or Flame AA for the following metals:

Aluminum	Chromium	Potassium
Antimony*	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

*NOTE: This microwave digestion method is not appropriate for the quantitative recovery of Antimony from soil and sediment samples.

2. SUMMARY OF METHOD

a. Water Sample Preparation

A representative 45 mL water sample is digested in 5 mL of concentrated nitric acid in a Teflon^{R} PFA vessel for 20 minutes using microwave heating. The digestate is then filtered to remove insoluble material. The sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

b. Soil Sample Preparation

A representative 0.5 g (wet weight) sample is digested in 10 mL of concentrated nitric acid in a Teflon^{R} PFA vessel for 10 minutes using microwave heating. The digestate is then filtered to remove insoluble material. The sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. NOTE: This microwave digestion method is not appropriate for the quantitative recovery of Antimony from soil and sediment samples.

3. APPARATUS AND MATERIALS

a. Commercial kitchen or home-use microwave ovens shall not be used for the digestion of samples under this contract. The oven cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.

b. Microwave oven with programmable power settings up to at least 600 Watts.

c. The system must use PFA Teflon^{R} digestion vessels (120 mL capacity) capable of withstanding pressures of up to 110 $\pm$10 psi (7.5 $\pm$0.7 atm). These vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

d. A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be a minimum of 3 rpm.

e. Polymeric volumetric ware in plastic (Teflon^{R} or polyethylene) 50 mL or 100 mL capacity.

f. Whatman No. 41 filter paper (or equivalent).

g. Disposable polypropylene filter funnel.

h. Analytical balance, 300 g capacity, and minimum $\pm$0.01 g.

i. Polyethylene bottles, 125 mL, with caps.

4. REAGENTS

a. ASTM Type II water (ASTM D1193): water must be monitored.

b. Sub-boiled, concentrated nitric acid (sp. gr. 1.41).

c. Concentrated hydrochloric acid (sp. gr. 1.19).

5. MICROWAVE CALIBRATION PROCEDURE

a. The calibration procedure is a critical step prior to the use of any microwave unit. The microwave unit must be calibrated every six months. The calibration data for each calibration must be available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined.

Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple-point calibration, then the point where linearity begins must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50 and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5 - 6 watts and becomes the smallest unit of power that can be controlled. If 20 - 40 watts are contained from 99-100%, that portion of the microwave

calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 Kg of water exposed to microwave radiation for a fixed period of time. The water is placed in a Teflon^{R} beaker (or a beaker that is made of some other material that does not adsorb microwave energy) and stirred before measuring the temperature. Glass beakers adsorb microwave energy and may not be used. The initial temperature of the water must be between 19 and 25 °C. The beaker is circulated continuously through the field for at least two (2) minutes at full power. The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature is recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements must be accurate to $\pm$ 0.1 °C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

The absorbed power is determined by the following formula:

$$P = \frac{(K)\ (Cp)\ (m)\ (DT)}{t}$$

Where:

P = The apparent power absorbed by the sample in watts (joules per second),

K = The conversion factor for thermochemical calories per second to watts (=4.184),

C_p = The heat capacity, thermal capacity, or specific heat (cal. $g^{-1}.°C^{-1}$) of water (=1.0),

m = The mass of the sample in grams (g),

DT = the final temperature minus the initial temperature (°C), and

t = the time in seconds (s)

Using 2 minutes and 1 Kg of distilled water, the calibration equation simplifies to:

P = (DT) (34.87).

The microwave user can now relate power in watts to the percent power setting of the microwave.

6. CLEANING PROCEDURE

a. The initial cleaning of the PFA vessels:

(1) Prior to first use - new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating the vessels for 96 hours at 200°C. The vessels must be disassembled during annealing and the sealing surfaces (the top of the vessel or its rim) must not be used to support the vessel during annealing.

(2) Rinse in ASTM Type I water.

(3) Immerse in 1:1 HCl for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

(4) Rinse in ASTM Type I water.

(5) Immerse in 1:1 HNO_3 for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

(6) The vessels are then rinsed with copious amounts of ASTM Type I water prior to use for any analyses under this contract.

b. Cleaning procedure between sample digestions

(1) Wash entire vessel in hot water using laboratory-grade nonphosphate detergent.

(2) Rinse with 1:1 nitric acid.

(3) Rinse three times with ASTM Type I water. If contaminants are found in the preparation blank, it is mandatory that steps a(2) through a(6) be strictly adhered to.

7. DIGESTION PROCEDURE

a. Water Sample Digestion Procedure

(1) A 45 mL aliquot of the sample is measured into Teflon^R digestion vessels using volumetric glassware.

(2) 5 mL of high purity concentrated HNO_3 is added to the digestion vessels.

(3) The caps with the pressure release valves are placed on the vessels hand tight and then tightened, using constant torque, to 12 ft./lbs. The weight of each vessel is recorded to 0.02 g.

(4) Place 5 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave.

(5) This procedure is energy balanced for five 45 mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than 5 samples are

digested, the remaining vessels must be filled with 45 mL of tap, DI or Type II water and 5 mL of concentrated nitric acid.

Newer microwave ovens may be capable of higher power settings which may allow a larger number of samples. If the analyst wishes to digest more than 5 samples at a time, the analyst may use different power settings as long as they result in the same time temperature conditions defined in the power programming for this method.

The initial temperature of the samples should be 24 $\pm$ 1°C. The preparation blank must have 45 mL of deionized water and the same amount (5 mL) of acid that is added to the samples.

The microwave unit first-stage program must be set to give 545 watts for 10 minutes and the second-stage program to give 344 watts for 10 minutes. This sequence brings the samples to 160 $\pm$4°C in ten minutes and permits a slow rise to 165-170 °C during the second 10 minutes.

(6) Following the 20 minute program, the samples are left to cool in the microwave unit for five minutes, with the exhaust fan ON. The samples and/or carousel may then be removed from the microwave unit. Before opening the vessels, let cool until they are no longer hot to the touch.

(7) After the sample vessel has cooled, weigh the sample vessel and compare to the initial weight as reported in the preparation log. Any sample vessel exhibiting a $\leq$ 0.5 g loss must have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with the sample preparation. Any sample vessel exhibiting a > 0.5 g loss must be identified in the preparation log and the sample redigested.

(9) Sample Filtration:

The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. The digestates are then filtered into 50 mL glass volumetric flasks through ultra-clean filter paper and diluted to 50 mL (if necessary). The samples are now ready for analysis. The sample results must be corrected by a factor of 1.11 in order to report final concentration values based on an initial volume of 45 mL. Concentrations so determined shall be reported as "total."

b. Soil Sample Digestion Procedure

(1) Add a representative 0.5 $\pm$0.050 grams of sample to the Teflon^R PFA vessel.

(2) Add 10 $\pm$0.1 mL of concentrated nitric acid. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel.

(3) Cap the vessel, then tighten using constant torque to 12 ft/lbs, according to the manufacturer's direction.

(4) Connect the sample vessel to the overflow vessel using Teflon^R PFA tubing.

(5) Weigh the vessel assembly to the nearest 0.01g.

(6) Place sample vessels in groups of 2 sample vessels or 6 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. If fewer than the recommended number of samples are to be digested (i.e., 3 samples plus 1 blank) then the remaining vessels must be filled with 10 mL of nitric acid to achieve the full complement of vessels.

Each sample vessel must be attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave. Connect the overflow vessel to the center well of the oven.

(7) The preparation blank must have 0.5 mL of deionized water and the same amount (10 mL) of acid that is added to the samples. The preparation blank must later be diluted to 50 mL in the same manner as the samples.

(8) Irradiate the 2 sample vessel group at 344 watts for 10 minutes, or the 6-sample vessel group at 574 watts for 10 minutes.

This program brings the samples to 175°C in 5.5 minutes; the temperature remains between 170-180°C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most samples. The pressure may exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases, the pressure will be limited by the relief pressure of the vessel to 7.5 $\pm$0.7 atm.

(9) Allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit, with exhaust fan ON. Allow the vessels to cool to room temperature before opening. The vessels must be carefully vented and uncapped in a fume hood.

(10) Weigh each vessel assembly. If the weight of acid plus the sample has decreased by more than 10% from the original weight, discard the digests. Determine the reason for the loss. Losses typically are attributed to use of digestion time longer than ten minutes, using too large of a sample, or having improper heating conditions. Once the source of the losses has been corrected, prepare a new set of samples for digestion.

(11) Sample Filtration:

Shake the sample well to mix in any condensate within the digestion vessel before being opened. Filter the digestion vessel into a 50 mL glass volumetric flask through ultra-clean filter paper. Rinse the sample digestion vessel, cap, connecting tube, and (if venting occurred) the overflow vessel into the 50 mL glass flask. Dilute to 50 mL. The samples are now ready for analysis. Concentrations so determined shall be reported as "total."

(12) Calculations:

The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/Kg)} = \frac{C \times V}{W \times S}$$

Where
C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample
S = % Solids/100

D. MERCURY AND CYANIDE PREPARATION

Refer to each specific method in this Exhibit for mercury and cyanide preparations.

SECTION IV

SAMPLE ANALYSIS

PART A - INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD

Method 200.7 CLP-M*
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD
FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

1. Scope and Application

1.1 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 4.)

1.2 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See 4.)

1.3 Table 1 lists elements along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detected limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.4 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by a photosensitive device. The photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The

*CLP-M modified for the Contract Laboratory Program.

possibility of additional interferences named in 4.1 (and tests for their presence as described in 4.2) should also be recognized and appropriate corrections made.

3. Safety

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

4. Interferences

4.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

4.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information, which was collected at the Ames Laboratory**, is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element.

The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table

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2, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed from the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths is not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

4.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift.

Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution has been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

4.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

4.2 Prior to reporting concentration data for the analyte elements, the Contractor shall analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis shall be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

5. Apparatus

5.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radio frequency generator.

5.1.3 Argon gas supply, welding grade or better.

5.2 Operating conditions -- Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

6. Reagents and Standards

6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

6.1.1 Acetic acid, conc. (sp gr 1.06).

6.1.2 Hydrochloric acid, conc. (sp gr 1.19).

6.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HC1 (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

6.1.4 Nitric acid, conc. (sp gr 1.41).

6.1.5 Nitric acid, (1+1): Add 500 mL conc. HNO_3 (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

6.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents and calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193.

6.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 hour at 105° C unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:

6.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolved 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HC1 and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HC1 and dilute to 1000 mL with deionized, distilled water.

6.3.2 Antimony solution stock, 1 mL = 100 ug Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HC1 and dilute to 1000 mL with deionized, distilled water.

6.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

6.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.6 Boron solution, stock, 1 mL = 100 ug B: Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

6.3.7 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.8 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.9 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.10 Cobalt solution stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

6.3.11 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.12 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HC1 and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.13 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL conc. HC1 and 1 mL conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

6.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.2043 g $(NH_4)2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

6.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1,000 mL with deionized, distilled water.

6.3.18 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.1907 g KC1, dried at 110°C, in deionized, distilled water. Dilute to 1,000 mL.

6.3.19 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

6.3.20 Silica solution, stock, 1 mL = 100 ug SiO_2: Do not dry. Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.21 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1,000 mL with deionized, distilled water.

6.3.22 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.2542 g NaC1 in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.23 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.24 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.3.25 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

6.4 Mixed calibration standard solutions -- Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 6.4.1 thru 6.4.5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See NOTE in 6.4.5.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see 6.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

6.4.1 Mixed standard solution I -- Manganese, beryllium, cadmium, lead, and zinc.

6.4.2 Mixed standard solution II -- Barium, copper, iron, vanadium, and cobalt.

6.4.3 Mixed standard solution III -- Molybdenum, silica, arsenic, and selenium.

6.4.4 Mixed standard solution IV -- Calcium, sodium, potassium, aluminum, chromium and nickel.

6.4.5 Mixed standard solution V -- Antimony, boron, magnesium, silver, and thallium.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

6.5 Two types of blanks are required for the analysis. The calibration blank (see Exhibit E) is used in establishing the analytical curve while the reagent blank (preparation blank, Exhibit E) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

6.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HC1 to 100 mL with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

6.5.2 The reagent blank (or preparation blank - see Exhibit E) must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6.6 In addition to the calibration standards, an instrument check standard, an interference check sample and a quality control sample are also required for the analyses (see Exhibit E).

6.6.1 The instrument check standard for continuing calibration verification is prepared by the analyst by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves.

6.6.2 The interference check sample is prepared by the analyst, or obtained from EPA if available.

6.6.3 The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier.

7. Procedure

7.1 Set up instrument with proper operating parameters established in Section 5.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

7.2 Initiate appropriate operating configuration of computer.

7.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 6.4. Flush the system with the calibration blank (6.5.1) between each standard. (NOTE: For boron concentrations greater than 500 ug/L extended flush times of 1 to 2 minutes may be required.)

7.4 Begin the sample run flushing the system with the calibration blank solution (6.5.1) between each sample. (See NOTE in 7.3.) Analyze the instrument check standard (6.6.1) and the calibration blank (6.5.1) each 10 analytical samples.

7.5 A minimum of two replicate exposures is required for standardization and all QC and sample analyses. The average result of the multiple exposures for the standardization and all QC and sample analyses shall be used.

8. Calculation

8.1 Reagent blanks (preparation blanks) shall be treated as specified in Exhibit E.

8.2 If dilutions were performed, the appropriate factor shall be applied to sample values.

8.3 Units shall be clearly specified.

9. Quality Control (Instrumental)

9.1 Quality control shall be performed as specified in Exhibit E.

TABLE 1 - RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength, nm(1)	Estimated Detection Limit, ug/L(2)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See(3)
Selenium	196.026	75
Silica ($Si0_2$)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

(1) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 4.1.1.) The use of alternate wavelengths must be reported (in nm) with the sample data.

(2) The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

(3) Highly dependent on operating conditions and plasma position.

TABLE 2. EXAMPLE OF ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

TABLE 3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes	(mg/L)	Interferents	(mg/L)
A1	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

PART B - ATOMIC ABSORPTION METHODS, FURNACE TECHNIQUE[+]

[+]From "Methods for Chemical Analysis of Water and Wastes" (EPA-600/4-79-020), Metals-4, as modified for use in the Contract Laboratory Program.

[*]CLP-M modified for the Contract Laboratory Program.

ANTIMONY

Method 204.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 20-300 ug/L
Approximate Detection Limit: 3 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized water. 1 mL = 1 mg Sb (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 800°C:
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is required.

3. Nitrogen may also be used as the purge gas.

4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.

5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

6. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

ARSENIC

Method 206.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 mL of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 mL conc. HNO_3 and dilute to 1 liter. 1 mL = 1 mg As (1000 mg/1).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 mL.
3. Nickel Nitrate Solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, and add 1 mL of conc. HNO_3, 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

Sample Preparation

1. Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

   Note: Another matrix modifier may be substituted for nickel nitrate if recommended by the instrument manufacturer. The matrix modifier used shall be reported in the SDG Case Narrative.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 1100°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe). If conditions occur where significant interference

*CLP-M modified for the Contract Laboratory Program.

is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.

3. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

4. If method of standard addition is required, follow the procedure given in Exhibit E.

5. The use of the Electrodeless Discharge Lamps (EDL) for the light source is recommended.

BERYLLIUM

Method 210.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-30 ug/L
Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 11.6586 g of beryllium sulfate, $BeSO_4$, in de-ionized distilled water containing 2 mL concentrated nitric acid and dilute to 1 liter. 1 mL = 1 mg Be (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 234.9 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

CADMIUM

Method 213.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 0.5-10 ug/L
Approximate Detection Limit: 0.1 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.282 g of cadmium sulfate, 3 $CdSO_4 \cdot 8$ H_2O (analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with deionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(NH_4)2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL.
3. Prepare dilutions of stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 500°C:
3. Atomizing Time and Temp: 10 sec @ 1900°C.
4 Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Contamination from the work area is critical in cadmium analysis. Use pipette tips which are free of cadmium.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

CHROMIUM

Method 218.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under Part C methods, AA Flame Technique.
2. Calcium Nitrate solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.
3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike, add 1 mL of 30% H_2O_2 and 1 mL of the calcium nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 357.9 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only.
2. Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/L where its suppressive effect becomes constant up to 1000 mg/L.
3. Background correction is required.
4. Nitrogen should not be used as a purge gas because of possible CN band interference.
5. Pipette tips have been reported to be a possible source of contamination.
6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
7. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

LEAD

Method 239.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 Liter with deionized distilled water. 1 mL = 1 mg Pb (1000mg/L).
2. Lanthanum Nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL conc. HNO_3 and dilute to 1000 mL with deionized distilled water. 1 mL = 50 mg La.
3. Working Lead solution: Prepare dilutions of stock lead solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard add 10 mL of the lanthanum nitrate solution.

Sample Preparation

1. To each 100 mL of prepared sample solution add 10 mL of the lanthanum nitrate solution.

   Note: Another matrix modifier may be substituted for lanthanum nitrate if recommended by the instrument manufacturer. The matrix modifier used shall be reported in the SDG Case Narrative.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 500°C:
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 283.3 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.

*CLP-M modified for the Contract Laboratory Program.

4. To suppress sulfate interference (up to 1500 ppm), lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p. 71, May-June 1976.)

5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.

6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

7. If method of standard addition is required, follow the procedure given in Exhibit E.

SELENIUM

Method 270.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 2 ug/L

Preparation of Standard Solution

1. Stock Selenium solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 mL. 1 mL = 1 mg Se (1000 mg/L).
2. Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2.6H_2O$ in deionized distilled water and make up to 100 mL.
3. Nickel Nitrate solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
4. Working Selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, and add 1 mL of conc. HNO_3, 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

Sample Preparation

1. Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

   Note: Another matrix modifier may be substituted for nickel nitrate if recommended by the instrument manufacturer. The matrix modifier used shall be reported in the SDG Case Narrative.

Instrument Parameters

1. Drying Time and Temp: 30 sec @ 125°C.
2. Charring Time and Temp: 30 sec @ 1200°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe). If conditions occur where significant interference

*CLP-M modified for the Contract Laboratory Program.

is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.

3. Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1% nickel.

4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).

5. If method of standard addition is required, follow the procedure given in Exhibit E.

6. The use of the Electrodeless Discharge Lamp (EDL) for the light source is recommended.

SILVER

Method 272.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-25 ug/L
Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated HNO_3 and make up to 1 liter. 1 mL = 1 mg Ag (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C:
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. The use of halide acids should be avoided.
4. If absorption to container walls or formation of AgC1 is suspected, see Exhibit D, Part C, Atomic Absorption Methods, Flame Technique.
5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

THALLIUM

Method 279.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.303 g of thallium nitrate, $T1NO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg T1 (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C:
3. Atomizing Time and Temp: 10 sec @ 2400°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

PART C - ATOMIC ABSORPTION METHODS, FLAME TECHNIQUE[+]

[+]From "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA EMSL, Cincinnati, Ohio, August 1977, Revised October 1980, as modified for use in the Contract Laboratory Program.

[*]CLP-M modified for the Contract Laboratory Program.

CALCIUM

Method 215.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.2-7 mg/L using a wavelength of 422.7 nm
Sensitivity: 0.08 mg/L
Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 g of $CaCO_3$ (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a minimum of dilute HC1. Dilute to 1000 mL with deionized distilled water. 1 mL = 0.5 mg Ca (500 mg/L).

2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 mL conc. HCl (Caution: Reaction is violent) and dilute to 500 mL with deionized distilled water.

3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each 10 mL of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 422.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium and nitrate cause no interference.

2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.

3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical inteferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter 14, 29 [1975])

4. The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

*CLP-M modified for the Contract Laboratory Program.

MAGNESIUM

Method 242.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.02-0.5 mg/L using a wavelength of 285.2 nm
Sensitivity: 0.007 mg/L
Detection Limit: 0.001 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 mL of redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 0.50 mg Mg (500 mg/L).

2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute to 500 mL with deionized distilled water.

3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 285.2 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/L.

2. The 202.5nm line may also be used. This line has a relative sensitivity of 25.

3. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/L), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

*CLP-M modified for the Contract Laboratory Program.

POTASSIUM

Method 258.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-2 mg/L using a wavelength of 766.5 nm
Sensitivity: 0.04 mg/L
Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 mL = 0.10 mg K (100 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 766.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. In air-acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks must be analyzed to correct for potassium impurities in the buffer zone.

2. The 404.4 nm line may also be used. This line has a relative sensitivity of 500.

3. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

* CLP-M modified for the Contract Laboratory Program.

SODIUM

Method 273.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.03-1 mg/L using a wavelength of 589.6 nm
Sensitivity: 0.015 mg/L
Detection Limit: 0.002 mg/L

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter. 1 mL = 1 mg Na (1000 mg/L).

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 589.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

2. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/L) to both standards and samples.

*CLP-M modified for the Contract Laboratory Program.

PART D - COLD VAPOR METHODS FOR MERCURY ANALYSIS

*CLP-M modified for the Contract Laboratory Program.

MERCURY ANALYSIS IN WATER BY MANUAL COLD VAPOR TECHNIQUE

MERCURY
Method 245.1 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in, or spiked to, a natural system.

1.2 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 mL sample, a detection limit of 0.2 ug Hg/L can be achieved (see 10.1).

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (Exhibit D, Section II).

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

*CLP-M modified for the Contract Laboratory Program.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place.

The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10^{o}C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (see Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hyroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate ($KMnO_4$): 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1 mL = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of conc. sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) to each bottle. Add 15 mL of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 PSI. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation.

The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as equal volumes of 0.1 M $KMnO_4$, and 10% H_2SO_4 or 0.25% iodine in a 3% a KI solution. A specially treated charcoal that will adsorb mercury vapor is commercially available.

8. Procedure

8.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle. Add 5 mL of conc. sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) mixing after each addition. Add 15 mL of potassium permanganate solution (6.5) to each sample bottle (see Note 6). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 6: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate (see Note 7). Purge the headspace in the BOD bottle for at least 1 minute and add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

NOTE 7: Add reductant in 6 mL increments until $KMnO_4$ is completely reduced.

9. Calculations

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\ Hg/L = \frac{ug\ Hg,\ curve}{aliquot\ volume,\ mL} \times \frac{1000\ mL}{1\ L}$$

10. Appendix

10.1 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/L, the standard deviations were $\pm$0.027, $\pm$0.0006, $\pm$0.01 and $\pm$0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

10.2 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water," p. 349, Method D3223 (1976).

MERCURY ANALYSIS IN WATER BY AUTOMATED COLD VAPOR TECHNIQUE

MERCURY
Method 245.2 CLP-M* (Automated Cold Vapor Technique)

1. Scope and Application

1.1 The working range is 0.2 to 20.0 ug Hg/L.

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

4. Interferences (see NOTE 1)

4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.

4.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.3 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All of the above interferences can be overcome by use of the Manual Mercury method.

*CLP-M modified for the Contract Laboratory Program.

5. Apparatus

5.1 Technicon Auto Analyzer or equivalent instrumentation consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator.

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (see Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 mL of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 mL conc. sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 mL of conc. nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate (See Note 3): Add 50 g stannous sulfate to 500 mL of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 4) Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium Permanganate ($KMnO_4$): 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g of potassium persulfate in 1 liter of distilled water.

6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 mL = 1.0 mg Hg.

6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/L.

6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure (See Note 5)

7.1 Set up manifold.

7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.

7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

7.4 Arrange working mercury standards from 0.2 to 20.0 ug Hg/L in sampler and start sampling. Complete loading of sample tray with unknown samples.

7.6 After the analysis is complete, put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as

equal volumes of 0.1 N $KMnO_4$(6.6) and 10% H_2SO_4 (6.1.2), or 0.25% iodine in a 3% KI solution, is recommended. A specially treated charcoal that will absorb mercury vapor is also available.

8. Calculations

8.1 Prepare a standard curve by plotting the peak height of processed standards against true concentration values. Use a linear regression equation to determine the concentration of field and QC samples by comparing the peak height of the samples with the peak height of the calibration standards.

8.2 If samples were diluted for analysis, multiply the results from the linear regression by the diluition factor.

MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

MERCURY (in Sediments)
Method 245.5 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.

1.2 The range of the method is 0.1 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control

2. Summary of Method

2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

2.2 An alternate digestion involving the use of an autoclave is described in 8.2.

3. Sample Handling and Preservation

3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.

3.2 Refrigerate solid samples at 4°C ($\pm$2°) upon receipt until analysis (see Exhibit D, Section II).

3.3 The sample should be analyzed without drying. A separate percent solids determination is required (Part F).

4. Interferences

4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.

4.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

*CLP-M modified for the Contract Laboratory Program.

5. Apparatus

5.1 Atomic Absorption Spectrophotometer (see Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows, may be used. Suitable cells may be constructed from pexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance. Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade of low mercury content.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid (6.1). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 3) Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL.

NOTE 3: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

6.5 Potassium Permanganate ($KMnO_4$): 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 = 1.0 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10 mL aliquots of the working mercury solutions (6.8) containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 mL. Add 5 mL of conc. H_2SO_4 (6.1) and 2.5 mL of conc. HNO_3 (6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 mL distilled water, 15 mL of $KMnO_4$ solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 mL of distilled water (final volume of distilled water = 100 mL). Treating each bottle individually, add 5 mL of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 4). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the

system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as: a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4, or b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is also commercially available.

8. Procedure

8.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a BOD bottle. Add enough distilled water to each sample to make a total volume of 10 mL. Add 5 mL of conc. sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) mixing after each addition. Heat two minutes in a water bath at 95°C. Cool, add 50 mL distilled water, 15 mL potassium permanganate solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 50 mL of distilled water (final volume of distilled water = 100 mL). Treating each bottle individually, purge the head space of the sample bottle for at least one minute and add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under 7.1.

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 mL of conc. H_2SO_4 and 2 mL of conc. HNO_3 are added to the 0.2 g of sample. 5 mL of saturated $KMnO_4$ solution and 8 mL of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 PSI for 15 minutes. Cool, make up to a volume of 100 mL with distilled water and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the headspace of the sample bottle for at least one minute and continue as described under 7.1.

9. Calculations

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\ Hg/g = \frac{ug/L\ Hg,\ curve}{aliquot\ dry\ wt.,\ g} \times final\ vol.\ after\ prep.,\ L$$

9.3 Report mercury concentrations as described for aqueous mercury samples converted to units of mg/kg. The sample result or the detection limit for each sample must be corrected for sample weight and % solids before reporting.

NOTE 5: ug/g is equivalent to mg/kg.

PART E - METHODS FOR TOTAL CYANIDE ANALYSIS

*CLP-M Modified for the Contract Laboratory Program.

METHOD FOR TOTAL CYANIDE ANALYSIS IN WATER

CYANIDE, TOTAL (in Water)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, and domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylaminobenzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.25 mg/250 mL of absorbing liquid) (Option A, 8.2).

1.3 The manual colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.01 mg/L (Option B, 8.3).

1.4 The working range of the semi-automated spectrophotometric method is 0.020 to 0.200 mg/L. Higher level samples must be diluted to fall within the working range (Option C, 8.4).

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

4.1 All bottles must be thoroughly cleansed and rinsed to remove soluble material from containers.

*CLP-M Modified for the Contract Laboratory Program.

4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

4.3 Samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH> 12) at the time of collection (Exhibit D, Section II).

4.4 Samples must be stored at 4°C(±2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in 8.1.

5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide as described in 4.3.

5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

6.1 Reflux distillation apparatus. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 mL (for titration)

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger (for manual spectrophotometric method).

6.4 Technicon AA II system or equivalent instrumentation (for automated spectrophotometric method) including:

6.4.1 Sampler

6.4.2 Pump III

6.4.3 Cyanide manifold

6.4.4 SCIC colorimeter with 15 mm flowcells and 570 nm filters

6.4.5 Recorder

6.4.6 Data system (optional)

6.4.7 Glass or plastic tubes for the sampler

7. Reagents

7.1 Distillation and Preparation Reagents

7.1.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.1.2 Cadmium carbonate: powdered

7.1.3 Ascorbic acid: crystals

7.1.4 Sulfuric acid: concentrated

7.1.5 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 mL flask, dissolve, and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$.

7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water.

7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).

7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).

7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 mL of acetone.

7.2.6 Sodium hydroxide solution, 0.25 N: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

7.3 Manual Spectrophotometric Reagents

7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in a liter of distilled water. Refrigerate this solution.

7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.3.3 Color Reagent-One of the following may be used:

7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.3.3.2 Pyridine-pyrazolone solution:

7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.3.3.2.2 3,3'Dimethyl-1,1'-diphenyl [4,4'-bi-2 pyrazolin]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily.

7.4.2 Phosphate buffer: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C(±2°C).

7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of concentrated HCl and mix. Dilute to about 900 mL with distilled water and mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C(±2°C).

7.4.4 Sampler wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

8.1.1 Place 500 mL of sample in the 1 liter boiling flask. Add 50 mL of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.3 Slowly add 25 mL concentrated sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

8.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.1.5 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

NOTE: The distillation procedure results in a 2x concentration of the sample.

8.2 Titrimetric Determination (Option A)

8.2.1 If the sample contains more than 1 mg of CN, transfer the distillate, or a suitable aliquot diluted to 250 mL, to a 500 mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 mL of sodium phosphate solution (7.3.1) and mix. The dilution factor must be reported on Form XIV.

8.3.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell. NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.3.2 Prepare a minimum of 3 standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Detection Limit (CRDL). To each standard, add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. The same method for color development (i.e., pyridine-barbituric acid or pyridine-pyrazolone) must be used for both the samples and standards. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

mL of Standard Solution (1.0 = 5 ug CN)	Conc. ug CN per 250 mL
0	Blank
0.5	2.5
1.0	5
5.0	25
10.0	50
15.0	75
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standard does not agree within $\pm$15% of the undistilled standards, the operator should find and correct the cause of the apparent error before proceeding.

8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL).

8.4 Semi-Automated Spectrophotometric Determination (Option C)

8.4.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/L, the following standards may be used:

mL Standard Solution (7.2.3) diluted to 1 liter	Concentration ug CN/L
0	0
2.0	10
4.0	20
10.0	50
20.0	100
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C)

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Re-establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. Calculations

9.1 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/L} = \frac{(A-B)\ 1{,}000\ \text{mL/L}}{\text{mL orig. sample}} \times \frac{250\ \text{mL}}{\text{mL of aliquot titrated}}$$

WHERE: A = volume of $AgNO_3$ for titration of sample (1 mL = 1 mg Ag)
B = volume of $AgNO_3$ for titration of blank (1 mL = 1 mg Ag)

AND: 250 mL = distillate volume (See 8.1.5)
1000 mL = conversion mL to L
mL original sample (See 8.1.1)
mL of aliquot titrated (See 8.2.1)

9.2 If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample, MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 mL and the distillate volume was 250 mL). Also, correct for, and report on Form XIV, any dilutions which were made before or after distillation.

The minimum concentration that can be reported from the calibration curve is 10 ug/L that corresponds to 5 ug/L in a sample that has been distilled.

9.3 If the manual spectrophotometric procedure is used, calculate the cyanide, in ug/L, in the original sample as follows:

$$\text{CN, ug/L} = \frac{A \times 1{,}000 \text{ mL/L}}{B} \times \frac{50 \text{ mL}}{C}$$

WHERE: A = ug CN read from standard curve (per 250 mL)
B = mL of original sample for distillation (See 8.1.1)
C = mL taken for colorimetric analysis (See 8.3.1)

AND: 50 mL = volume of original sample aliquot (See 8.3.1)
1000 mL/L = conversion mL to L

The minimum value that can be substituted for A is 2.5 ug per 250 mL. That yields a concentration of 5 ug/L in the distilled sample.

METHOD FOR TOTAL CYANIDE ANALYSIS IN SOIL/SEDIMENT

CYANIDE, TOTAL (in Sediments)
Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric;Semi-Automated Spectrophotometric)

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in sediments and other solids.

1.2 The detection limit is dependent upon the weight of sample taken for analysis.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone for 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

4.1 Samples must be stored at 4°C(±2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.

4.2 Samples are not dried prior to analysis. A separate percent solids determination must be made in accordance with the procedure in Part F.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in 8.1.

5.2 Sulfides adversely affect the colorimetric and titration procedures.

*CLP-M Modified for the Contract Laboratory Program.

5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as DOW Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

6.1 Reflux distillation apparatus. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 mL (for titration)

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 Technicon AA II system or equivalent instrumentation (for automated spectrophotometric method) including:

6.4.1 Sampler

6.4.2 Pump III

6.4.3 Cyanide manifold

6.4.4 SCIC colorimeter with 15 mm flowcells and 570 nm filters

6.4.5 Recorder

6.4.6 Data system (optional)

6.4.7 Glass or plastic tubes for the sampler

7. Reagents

7.1 Distillation and Preparation Reagents

7.1.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.1.2 Cadmium carbonate: powdered

7.1.3 Ascorbic acid: crystals

7.1.4 Sulfuric acid: concentrated

7.1.5 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 mL flask, dissolve and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g of KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$.

7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water (1 mL = 50.0 ug).

7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).

7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).

7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 mL acetone.

7.3 Manual Spectrophotometric Reagents

7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.3.3 Color reagent - One of the following may be used:

7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.3.3.2 Pyridine-pyrazolone solution:

7.3.3.2.1 3-Methyl-l-phenyl-2-pyrazolin-5- one reagent, saturated solution: Add 0.25 g of 3-methyl-l-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.3.3.2.2 3,3'Dimethyl-l,1'-diphenyl-[4,4'-bi-2-pyrazolin]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with

cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily.

7.4.2 Phosphate Buffer: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C.

7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of conc. HCl mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.

7.4.4 Sampler Wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

8.1.1 Accurately weigh a representative 1-5 g portion of wet sample and transfer it to a boiling flask. Add 500 mL of distilled water. Shake or stir the sample so that it is dispersed.

8.1.2 Add 50 mL of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.

8.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.4 Slowly add 25 mL of conc. sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

8.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.1.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

NOTE: The distillation procedure results in a 2x concentration of the sample.

8.2 Titrimetric Determination (Option A)

8.2.1 If the sample contains more than 1 mg of CN, transfer the distillate, or a suitable aliquot diluted to 250 mL, to a 500 mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (7.1.1). Add 15.0 mL of sodium phosphate solution (7.3.1) and mix.

8.3.1.1 Pyridine-barbituric acid method: Add 2 mL of Chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes add 5 mL of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell.

NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.3.2 Prepare a minimum of three standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks. NOTE: One calibration standard must be made at the CRDL. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. The same method for color development (i.e., pyridine-barbituric acid or pyridine-pyrazolone) must be used for both the samples and standards. Standards must bracket the concentrations of the sample. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

mL of Standard Solution (1.0 = 5 ug CN)	Conc. ug CN per 250 mL
0	Blank
0.5	2.5
1.0	5
5.0	25
10.0	50
15.0	75
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standard does not agree within ±15% of the undistilled standards the operator should find and correct the cause of the apparent error before proceeding.

8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL).

8.4 Semi-Automated Spectrophotometric Determination (Option C)

8.4.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/L, the following standards may be used:

mL Standard Solution (7.2.3) diluted to 1 liter	Concentration ug CN/L
0	0
2.0	10
4.0	20
10.0	50
20.0	100
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C).

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL

dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Reestablish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. Calculations

9.1 A separate determination of percent solids must be performed (see Part F).

9.2 The concentration of cyanide in the sample is determined as follows.

9.2.1 (Titration)

$$CN,\ mg/kg = \frac{(A - B) \times \frac{250\ mL}{mL\ aliquot\ titrated} \times 1000\ g/kg}{C \times \frac{\%solids}{100}}$$

WHERE: A = mL of $AgNO_3$ for titration of sample (1 mL = 1 mg Ag)
B = mL of $AgNO_3$ for titration of blank (1 mL = 1 mg Ag)
C = wet weight of original sample in g (See 8.1.1)

AND: 250 mL = volume of distillate (See 8.1.6)
1000 g/kg = conversion factor g to kg
mL aliquot titrated (See 8.2.1)
% solids (see Part F)

9.2.2 (Manual Spectrophotometric)

$$CN,\ mg/kg = \frac{A \times \frac{50\ mL}{B}}{C \times \frac{\%\ solids}{100}}$$

WHERE: A = ug CN read from standard curve (per 250 mL)
B = mL of distillate taken for colorimetric determination (8.3.1)
C = wet weight of original sample in g (See 8.1.1)

The minimum value that can be substituted for A is 2.5 ug/250 mL. That yields a concentration of 5 ug/L in the distilled sample.

AND: 50 mL = volume of standard taken for colorimetric determination (See 8.3.1)
% solids (see Part F)

9.2.3 (Semi-Automated Spectrophotometric)

If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the

samples and QC audits to determine the cyanide concentration in the distillates.

$$CN, mg/kg = \frac{A \times .25}{C \times \frac{\% \text{ solids}}{100}}$$

WHERE: A = ug/L determined from standard curve
C = wet weight of original sample in g (See 8.1.1)

AND: .25 = conversion factor for distillate final volume (See 8.1.6)
% solids (see Part F)

The minimum value that can be substituted for A is 2.5 ug/250 mL.

METHOD FOR TOTAL CYANIDE ANALYSIS BY MIDI DISTILLATION

CYANIDE, TOTAL (water and soils)

Method 335.2 CLP-M (Semi-automated Spectrophotometric)

1. Scope and Application

1.1 Cyanide determined by this method is defined as cyanide ion and complex cyanides converted to hydrocyanic acid by reaction in a reflux system with mineral acid in the presence of magnesium ion.

1.2 This method covers the determination of cyanide by midi distillation with a semi-automated colorimetric analysis of the distillate.

1.3 The detection limit for the semi-automated colorimetric method is approximately 10 ug/L.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a midi reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH less than 8 without hydrolysis to the cyanate. After the reaction is complete, color is formed on the addition of pyridinebarbituric acid reagent. The absorbance is read at 580 nm. To obtain colors of comparable intensity, it is essential to have the same salt content in both the samples and the standards.

3. Sample Handling and Preservation

3.1 All bottles must be thoroughly cleansed and rinsed to remove soluble materials from containers.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-Starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add additional 0.6 g of ascorbic acid for each liter of sample volume.

3.3 Samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH > 12) at the time of collection.

3.4 Samples must be stored at 4°C(±2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.

4. Interferences

4.1 Interferences are eliminated or reduced by using the distillation procedure.

4.2 Sulfides adversely affect the colorimetric procedures. If a drop of distillate on lead acetate test paper indicates the presence of sulfides, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

4.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoaming agent will prevent the foam from collecting in the condenser.

5. Apparatus

5.1 Midi reflux distillation apparatus.

5.2 Heating block - Capable of maintaining 125°C ±5°C.

5.3 Auto analyzer system with accessories:

5.3.1 Sampler

5.3.2 Pump

5.3.3 Cyanide cartridge

5.3.4 Colorimeter with 50 mm flowcells and 580 nm filter

5.3.5 Chart recorder or data system.

5.4 Assorted volumetric glassware, pipets, and micropipets.

6. Reagents

6.1 Distillation and Preparation Reagents

6.1.1 Sodium hydroxide absorbing solution and sample wash solution, 0.25 N: Dissolve 10.0 g NaOH in ASTM Type II water and dilute to one liter.

6.1.2 Magnesium chloride solution, 51% (w/v): Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in ASTM Type II water and dilute to one liter.

6.1.3 Sulfuric acid, 50% (v/v): Carefully add a portion of concentrated H_2SO_4 to an equal portion of ASTM Type II water.

6.1.4 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in ASTM Type II water and dilute to one liter.

6.2 Standards

6.2.1 Stock cyanide solution, 1000 mg/L CN: Dissolve 2.51 g of KCN and 2.0 g KOH in ASTM Type II water and dilute one liter. Standardize with 0.0192 N $AgNO_3$.

6.2.2 Intermediate cyanide standard solution, 10 mg/L CN: Dilute 1.0 mL of stock cyanide solution (6.2.1) plus 20 mL of 1.25 N NaOH solution (6.1.4) to 100 mL with ASTM Type II water. Prepare this solution at time of analysis.

6.2.3 Rhodamine indicator: Dissolve 20 mg of p-dimethylamino-benzal-rhodamine in 100 mL acetone.

6.2.4 Silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to a constant weight at 104°C. Weigh out 3.2647 g of dried $AgNO_3$ and dissolve in ASTM Type II water. Dilute to one liter (1 mL corresponds to 1 mg CN).

6.2.5 Potassium chromate indicator solution: Dissolve 50 g K_2CRO_4 in sufficient ASTM Type II water. Add silver nitrate solution until a definite red precipitate is formed. Let stand for at least 12 hours, filter, and dilute to one liter with ASTM Type II water.

6.2.6 Primary standard sodium chloride, 0.0141 N: Dissolve 824.1 mg NaCl (NBS-dried 20 minutes at 104°C) in ASTM Type II water and dilute to one liter.

6.2.7 Sodium hydroxide solution, 0.1 N: Dissolve 4 g of NaOH in ASTM Type II water and dilute to one liter.

6.3 Semi-Automated Spectrophotometric Reagents

6.3.1 Phosphate buffer solution, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in ASTM Type II water and dilute to one liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C.

6.3.2 Chloramine-T solution, 0.4% (w/v): Dissolve 0.4 g of chloramine-T in ASTM Type II water and dilute to 100 mL. Prepare fresh at time of analysis.

6.3.3 Color reagent solution, pyridine barbituric acid color reagent solution: Prepare this solution in the hood. Transfer 15 g of barbituric acid into a one liter Erlenmeyer flask. Add about 100 mL of ASTM Type II water and swirl the flask to mix. Add 75 mL of pyridine and 15 mL concentrated HCl and mix until all the barbituric acid is dissolved. Dilute to one liter with ASTM Type II water and store at 4°C.

7. Procedure

7.1 Distillation

7.1.1 The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 50 mL or less for aqueous samples and one gram for solid materials. NOTE: All samples must initially be run undiluted (i.e., aqueous samples must first be run with a 50 mL aliquot and solid samples using a one gram sample). When the cyanide concentration exceeds the highest calibration standard, appropriate dilution (but not below the CRDL) and reanalysis of the sample are required. The dilution factor must be reported on Form XIV.

7.1.2 For aqueous samples: Pipet 50 mL of sample, or an aliquot diluted to 50 mL, into the distillation flask along with 2 or 3 boiling chips.

7.1.3 For solid samples: Weigh 1.0 g of sample (to the nearest 0.01 g) into the distillation flask and dilute to 50 mL with ASTM Type II water. Add 2 or 3 boiling chips.

7.1.4 Add 50 mL of 0.25 N NaOH (6.1.1) to the gas absorbing impinger.

7.1.5 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5 N NaOH.

7.1.6 Turn on the vacuum and adjust the gang (Whitney) values to give a flow of three bubbles per second from the impingers in each reaction vessel.

7.1.7 After five minutes of vacuum flow, inject 5 mL of 50% (v/v) H_2SO_4 (6.1.3) through the top air inlet tube of the distillation head into the reaction vessel. Allow to mix for 5 minutes. NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

7.1.8 Add 2 mL of magnesium chloride solution (6.1.2) through the top air inlet tube of the distillation head into the reaction flask. Excessive foaming from samples containing surfactants may be quelled by the addition of another 2 mL of magnesium chloride solution.

7.1.9 Turn on the heating block and set for 123-125°C. Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

7.1.10 After one and a half hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

7.1.11 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed. The solutions must be analyzed for cyanide within the 12 day holding time specified in Section II.

7.2 Semi-Automated Spectrophotometric Determination

7.2.1 Operating conditions: Because of the difference between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. The analyst should follow the instructions provided by the manufacturer of the particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

The following general procedure applies to most semi-automated colorimeters. Set up the manifold and complete system per manufacturer's instructions. Allow the colorimeter and recorder to warm up for at least 30 minutes prior to use. Establish a steady reagent baseline, feeding ASTM Type II water through the sample line and appropriate reagents (6.3) through reagent lines. Adjust the baseline using the appropriate control on the colorimeter.

7.2.2 Prepare a minimum of 3 standards and a blank by pipetting suitable volumes of standard solution into 50 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Detection Limit (CRDL).

As an example, standard solutions could be prepared as follows:

Total ug CN standard solution	mL 10 mg/L CN	mL 0.05 N NaOH
0.00	0.000	20
0.10	0.010	20
0.25	0.025	20
0.50	0.050	20
1.00	0.100	20
2.00	0.200	20
5.00	0.500	20
10.00	1.000	20

7.2.2.1 Dilute standards to 50 mL using ASTM Type II water. It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve for each SDG to ensure the distillation technique is reliable. If the distilled standard does not agree within $\pm$15% of the undistilled standards, the operator must find and correct the cause of the error before proceeding.

7.2.3 Aspirate the highest calibration standard and adjust the colorimeter until the desired (maximum) signal-range is obtained.

7.2.4 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

7.2.5 Switch sample line from the ASTM Type II water to sampler, set the appropriate sampling rate and begin the analysis.

8. Calculations

8.1 Calculations for Semi-automated Colorimetric Determination

8.1.1 Prepare a standard curve by plotting absorbance (peak heights, determined visually or using a data system) of standards (y) versus cyanide concentration values (total ug CN/L) (x). Perform a linear regression analysis.

8.1.2 Multiply all distilled values by the standardization value to correct for the stock cyanide solution not being exactly 1000 mg/L (See 6.2.1).

8.1.3 Using the regression analysis equation, calculate sample receiving solution concentrations from the calibration curve.

8.1.4 Calculate the cyanide of aqueous samples in ug/L of original sample, as follows:

$$\text{CN, ug/L} = \frac{A \times D \times F}{B}$$

where:
A = ug/L CN of sample from regression analysis
B = Liter of original sample for distillation (0.050 L) (See 7.1.2)
D = any dilution factor necessary to bracket sample value within standard values
F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is 10 ug/L.

8.1.5 Calculate the cyanide of solid samples in mg/kg of original sample, as follows:

8.1.5.1 A separate determination of percent solids must be performed (See Part F).

8.1.5.2 The concentration of cyanide in the sample is determined as follows:

$$\text{CN, mg/kg} = \frac{A \times D \times F}{B \times E}$$

where:
A = ug/L CN of sample from regression analysis curve

B = wet weight of original sample in g (See 7.1.3)

D = any dilution factor necessary to bracket sample value within standard values

E = % solids (See Part F)/100.

F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is 10 ug/L.

PART F - PERCENT SOLIDS DETERMINATION PROCEDURE

1. Immediately following the weighing of the sample to be processed for analysis (see Section III, Part B- Soil/Sediment Sample Preparation), add 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.

2. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105°C. Sample handling and drying should be conducted in a well-ventilated area.

3. Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.* Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.

4. Duplicate percent solids determinations are required at the same frequency as are other analytical determinations. Duplicate results are to be recorded on FORM VI-IN.

5. For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.

6. Calculate percent solids by the formula below. The value thus obtained will be reported on the appropriate FORM I-IN and, where applicable, FORM VI-IN . This value will be used for calculating analytical concentration on a dry weight basis.

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

*For the purpose of paragraph 3, drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12 hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.